Claims

1. Polymer electrolyte for an electrochemical generator based on:

- at least one four branched polymer preferably having hybrid terminations, more preferably hybrid acrylate (preferably methacrylate) and alkoxy (preferably alkoxy having 1 to 8 carbon atoms, still more preferably methoxy or ethoxy), or vinyl terminations, at least one branch of said four branched polymer (and preferably at least two branches) being capable of giving rise to cross-linking;
- at least one component selected from the following families:
  - poly(vinylyldienefluorides), also called (PVDF), of chemical formula $(CH_2\text{-}CF_2)_n$, where n preferably varies between 1,000 and 4,000, preferably such that n is near 150, preferably those having an average molecular weight between 10,000 and 1 million, more preferably still those having an average molecular weight between 100,000 and 250,000;
  - poly(vinylydiene fluoro-co-hexafluoropropene) copolymers, of formula $[(CH_2\text{-}CF_2)_x(CF_2\text{-}CF(CF_3))_{1-x}]_n$ also called (PVDF-HFP), wherein n varies between 1,000 and 4,000, preferably n varies from 2,000 to 3,000, more preferably still n is near 150 and x varies preferably between 0.12 and 0.5, preferably those having an average molecular weight between 10,000 and 1 million, more

preferably still those having an average molecular weight between 100,000 and 250,000;

- poly(tetrafluoroethylenes), also called (PTFE), of chemical formula $(CF_2\text{-}CF_2)_n$, wherein n varies from 5 to 20,000, preferably n varies from 50 to 10,000, preferably those having an average molecular weight between 500 and 5 million, more preferably still those having an average molecular weight between 5,000 and 1,000,000, preferably about 200,000;
- poly(ethylene-co-propylene-co-5-methylene-2-norbornenes) or ethylene propylene-diene copolymers, also called EPDM, preferably those having an average molecular weight between 10,000 and 250,000, preferably between 20,000 and 100,000;
- polyols, preferably polyols such as:
  - polyvinyl alcohol having an average molecular weight preferably between 50,000 and 1 million, or a cellulose, preferably having an average molecular weight between 5,000 and 250,000 in which part of the OH groups are replaced by OCH_3, OC_2H_5, OCH_4OH, $OCH_2CH(CH_3)OH$, $OC(=O)CH_3$, or $OC(=O)C_2H_5$, and/or
  - ethylene oxide condensation products, preferably those having an average molecular weight between 1,000 and 5,000, preferably pure or in admixture with propylene oxide on glycerol or trimethylolpropane, and possibly cross-linked with

a di or tri-isocyanate of formula $(O=C=N)_x$-R in which 2<x<4 and R represents an aryl or alkyl group ensuring polyfunctionality with the group $(O=C=N)_x$;

- poly(methylmethacrylates) also called (PMMA), of formula $[(CH_2\text{-}C(CH_3)/(CO_2CH_3)]_n$ wherein n preferably varies between 100 and 10,000, more preferably still n varies from 500 to 5,000, preferably those having an average molecular weight between 10,000 and 1 million, preferably those having an average molecular weight between 50,000 and 500,000;
- poly(acrylonitriles), also called (PAN), of chemical formula $[(CH_2\text{-}CH(CN)]_n$ in which n varies from 150 to 18,800, more preferably still n varies from 300 to 4,000, preferably those having an average molecular weight between 10,000 and 1 million, more preferably still those having an average molecular weight between 20,000 and 200,000;
- SiO_2-Al_2O_3; and
- nano TiO_2 non coated or coated with an organic material that is preferably compatible (i.e. stable and/or generating no secondary parasite reaction), with one or more of the polymers defined in columns 1 and 2 of US-A-6,190,804 Patent, the organic material preferably being selected from the group comprising at least one polyol and/or one polyethylene-polyoxyethylene copolymer and/or one inorganic material that is preferably SiO_2 and/or Al_2O_3.

2. Polymer electrolyte according to claim 1, additionally containing a salt, preferably a lithium salt such as LiTFSI, or a mixture of salts with a plasticizing agent.

3. Polymer electrolyte according to claim 2, in dry form (free solvent), obtained by adding a lithium salt or a mixture of salts (in the matrix) of the polymer in order to provide ionic conductivity.

4. Polymer electrolyte according to claim 3, in which the lithium salts are of the type: $LiN(SO_2CF_3)_2$; LiTFSI, $LiN(SO_2C_2F_5)_2$; BETI, $LiC(SO_2CF_3)_3$, $LiBF_4$, $LiPF_6$, LiCLO4, $LiSO_3CF_3$, $LiAsF_6$.

5. Polymer electrolyte according to any one of claims 2 to 5, in which the plasticizing agent consists of at least one mixture of organic solvent preferably selected from the group consisting of: an ethylene carbonate, a propylene carbonate, a γ-gamma butyrolactone, a dimethyl carbonate, a diethyl carbonate, a tetra ethyl-sulfone amide, and a methyl-ethyl carbonate (EMC).

6. Electrolytic composition obtained from at least one polymer electrolyte according to any one of claims 1 to 5, by subjecting the components of said electrolyte to conditions allowing cross-linking of the polymer.

7. Electrolytic composition according to claim 6, in which the cross-linking is obtained by UV, heat treatment and/or electron beam (EB).

8. Electrolytic composition according to claim 6 or 7, in which the cross-linking is carried out in the presence of at least one lithium salt.

9. Electrolytic composition according to claim 6 or 7, in which the cross-linking is carried out in the absence of lithium salts.

10. Electrolytic composition according to any one of claims 6 to 9, obtained by cross-linking carried out at a temperature between 50 and 100° C, preferably at a temperature between 60 and 80° C.

11. Electrolytic composition according to any one of claims 1 to 10, obtained by cross-linking for a duration between 5 minutes and 8 hours, preferably for a duration between 1 hour and 4 hours.

12. Electrolytic composition according to any one of claims 1 to 11, obtained by cross-linking in the presence of a catalyst selected from the group consisting of organic peroxides, hydroperoxides or peresters, preferably the catalyst is selected from the group consisting of organic peroxides.

13. Electrolytic composition according to any one of claims 6 to 12, in which the cross-linking is carried out by heat treatment *in situ* in a battery or in a once built hybrid super condenser and containing said electrolytic composition.

14. Electrolytic composition according to any one of claims 6 to 13, in the form of a polymer gel.

15. Electrolytic composition according to any one of claims 6 to 13 in solid form.

16. Electrochemical device (preferably battery, super condenser or hybrid super condenser) comprising:

- at least one electrolyte such as defined in any one of claims 1 to 5 and/or at least an electrolytic composition according to any one of claims 6 to 15;
- an electroactive anode, preferably of the type $Li_4Ti_5O_{12}$, and
- a cathode of the 3.5 to 5 volt type such as those prepared from $LiCoPO_4$ and/or of $Li(Mn_{0.66}Ni_{0.34})O_2$ or the like.

17. Super condenser according to claims 16 comprising:
    - at least one polymer electrolyte according to any one of claims 1 to 5 or at least one electrolytic composition according to any one of claims 6 to 15;
    - an electroactive anode preferably of the $Li_4Ti_5O_{12}$ type; and
    - a electroactive cathode preferably of the large surface area carbon type.

18. Super condenser according to claim 17, in which carbon is in the form of particles having a specific surface higher than or equal to 2 m^2/g and lower than or equal to 2500 m^2/g, preferably carbon is in the form of particles having a specific surface higher than or equal to 50 m^2/g, preferably between 50 and 2400 m^2/g.

19. Super condenser according to claim 17 or 18, in which the electroactive cathode is of the conducting polymer type and preferably consists of at least one conducting polymer at high voltage such as a polyaniline and/or such as a polythiophene and/or such as an arylthiophene, preferably selected from 3-arylthiophenes.

20. Super condenser according to any one of claims 16 to 19, in which the electroactive anode is of the GIC type (Graphite Intercalation Compound), preferably made of natural and/or synthetic graphite, and/or of highly crystalline carbon, preferably the carbon is treated before being

used to constitute the electrode, at temperatures > 2000° C (two thousand degrees Celsius).

21. Super condenser according to any one of claims 17 to 20, in which the electroactive anode consists of a layer of carbon of low crystalline type, preferably of a carbon treated at temperatures lower than or equal to 2000° C and/or a hard carbon.

22. Electrochemical device according to claim 16 or a super condenser according to any one of claims 17 to 21, in which the electroactive anode is of the lithium alloy type, such as AlLi and/or $Li_{4.4}Sn_{22}$ or the like.

23. Electrochemical device according to claim 16 or a super condenser according to any one of claims 17 to 22, in which the electroactive cathode is of the 4 volt type and is preferably constituted from at least one oxide selected from the group consisting of $LiCoO_2$, $LiMn_2O_4$. $LiNiO_2$ and compounds involving redox couples of these elements, alone or as a mixture.

24. Electrochemical device according to claim 16 or a super condenser according to any one of claims 17 to 21, in which the electroactive anode is of the GIC (Graphite Intercalation Compound) type, made of natural and /or synthetic graphite, and/or of carbon with high crystallinity, preferably the carbon is heat treated at temperatures higher than or equal to 2000° C.

25. Electrochemical device according to claim 16 or a super condenser according to any one of claims 17 to 21, in which the electroactive anode consists of a carbon with low cristallinity preferably of a carbon that is treated at temperatures < 2000° C.

26. Supercapacity or device according to claim 16, in which the electroactive anode is of the lithium allow type, such as AlLi and/or $Li_{4.4}Sn_{22}$ or the like.

27. Supercapacity according to any one of claims 18 to 26, in which, the electroactive anode is of the metallic lithium type.

28. Electrochebemical device being stable during cycling as determined according to the method defined in the description on page 17 that is higher than 4 volts.

29. Super condenser according to claim 28.